

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2002 (27.12.2002)

PCT

(10) International Publication Number
WO 02/102496 A1

(51) International Patent Classification⁷: **B01D 53/14**,
53/18, C07D 301/32

(21) International Application Number: PCT/EP02/06448

(22) International Filing Date: 10 June 2002 (10.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01114576.0 18 June 2001 (18.06.2001) EP

(71) Applicants: **DEGUSSA AG** [DE/DE]; Bennigsenplatz
1, 40474 Düsseldorf (DE). **UHDE GMBH** [DE/DE];
Friedrich-Uhde-Strasse 15, 44141 Dortmund (DE).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,
YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(72) Inventors: **HOFEN, Willi**; Südring 54, 63517 Rodenbach
(DE). **THIELE, Georg**; Julius-Leber-Strasse 6, 63450
Hanau (DE). **WOELL, Wolfgang**; Backesweg 28a, 63477
Maintal (DE).

(74) Agent: **STERNAGEL, FLEISCHER, GODEMEYER
& PARTNER**; Braunsberger Feld 29, 51429 Bergisch
Gladbach (DE).

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

WO 02/102496 A1

(54) Title: PROCESS FOR THE RECOVERY OF COMBUSTIBLE COMPONENTS OF A GAS STREAM

(57) Abstract: The present invention refers to a process for the recovery of combustible components of a gas stream comprising the combustible components and oxygen by selective absorption of the combustible components in a solvent, whereby during the absorption the gas phase is dispersed in a continuous liquid phase of the solvent. In a preferred embodiment the present invention refers to a process for the epoxidation of propene with hydrogen peroxide in an alcoholic solvent in presence of a catalyst, wherein a gas stream comprising unreacted propene, propene oxide and oxygen from the decomposition of the hydrogen peroxide is separated from the reaction mixture and the combustible components in said gas stream are recovered using a process as described above.

Process for the Recovery of Combustible Components of a Gas Stream

The present invention refers to a process for the recovery of combustible components of a gas stream comprising the combustible components and oxygen by selective absorption of the combustible
5 components in a solvent. The present invention in particular refers to a process for recovery of combustible components from an exit gas stream from an oxidation reaction with a peroxide component, whereby due to the decomposition of the peroxide oxygen is accumulated during the oxidation
10 reaction. The present invention is particularly suitable for a working-up stage in a process for epoxidation of olefins.

In numerous processes involving oxidation with peroxide compounds, particularly hydrogen peroxide, gas mixtures are formed that comprise
15 considerable amounts of organic combustible components in addition to molecular oxygen resulting from the decomposition of the peroxide compounds. For safety reasons, these processes have to be conducted to ensure that the oxygen content is below the explosion limit. For economic reasons, it is often necessary to recover the combustible
20 components of an exit gas stream, since they may contain valuable compounds like, for example, product compounds or components that can be recycled to the initial reaction stage. Therefore, it has been proposed to recover the combustible components by selective absorption in a suitable solvent.

25

The oxygen content of the gas phase increases within the absorption unit due to the absorption of organic combustible components in the solvent. This may have the consequence that even if the gas stream entering the absorption unit is not an ignitable composition, it may become ignitable
30 during the process of absorption. Therefore, for safety reasons, an inert gas is introduced in the absorption unit to avoid, under any

condition, the formation of an ignitable composition within the absorption unit.

- For example, EP-A-719 768 describes a process for the epoxidation of an olefin with hydrogen peroxide, wherein a gas mixture of the olefin and oxygen from hydrogen peroxide decomposition is separated from the liquid epoxidation reaction mixture and the olefin is absorbed from the gas mixture in a liquid absorbent and inert gas is added to the oxygen in an amount sufficient to prevent formation of a flammable gas composition.
- Referring to the example in EP-A-719 768 the absorption liquid is introduced into the upper section and the gaseous purge stream into the lower section of the absorption zone to ensure a counter-current flow. But there is no indication whether the liquid phase or the gas phase is the continuous phase.
-

15

- EP-A-583 828 discloses a process for ethylene recovery in a process of direct oxidation of ethylene oxide. According to this process the direct-oxidation product is worked up in three different stages. In the third stage unreacted ethylene is removed by absorption using a high molecular weight organic liquid for example paraffins. From the information given for performing the absorption it is not evident that the gas phase is dispersed in a continuous liquid phase. On the contrary the information that the contacting surface may be created by trays, structured packing or random dump packing implies to the person skilled in the art that the gas phase is the continuous phase and the liquid phase is the dispersed phase since otherwise the contacting surface between gas and liquid phase cannot be increased using packings in the absorber column.
- Similarly, European Patent Application 00102542.8 discloses a process for the working-up of an exit gas stream from the epoxidation of an olefin with hydrogen peroxide, comprising olefin oxide, unreacted

olefin, and oxygen, whereby the exit gas stream is brought into contact in an absorption unit with the same solvent as used in the epoxidation stage, and a solvent stream loaded with olefin and olefin oxide is drawn off from the absorption unit, and an exit gas stream containing oxygen
5 is discharged. Additionally, an inert gas stream is introduced into the absorption unit, wherein the inert gas leaves the absorption unit together with the oxygen in the exit gas stream. The quantity of inert gas introduced is preferably selected as a function of the quantity and composition of the exit gas stream leaving the reaction stage, such that
10 the exit gas stream leaving the absorption unit is no longer an ignitable composition. Thereby, measures are taken to avoid at any stage within the absorption unit the presence of an ignitable composition.

There is a considerable drawback associated with this procedure. Due to
15 the addition of inert gas, the total gas stream within the absorption unit is drastically increased. Thereby, the efficiency of the absorption is reduced and larger absorption units and larger amounts of absorbing solvents are necessary to achieve the desired separation of valuable organic components from the exit gas stream of a reaction zone.

20 Thus, the object of the present invention is to provide a process for the recovery of combustible compounds of a gas stream comprising combustible components and oxygen that does not have the above discussed disadvantages while ensuring safety of the overall process.

25 This object has been attained by a process for the recovery of combustible components of a gas stream comprising the combustible components and oxygen by selective absorption of the combustible components in a solvent, whereby during the absorption the gas phase is
30 dispersed in a continuous liquid phase of the solvent.

- The present inventors have surprisingly discovered that if the gas phase comprising combustible components and oxygen is dispersed in a continuous liquid phase of the solvent during absorption, even if due to the depletion of combustible components from the gas phase the oxygen concentration in the gas phase rises above the explosion limit, the gas phase still cannot be ignited within the absorption unit because the gas phase is finely dispersed in the continuous liquid phase of the solvent. Consequently, addition of inert gas to the gas phase prior to entering the absorption unit or within the absorption zone in the absorption unit is not necessary any longer. Thus, it is preferred that neither prior to entering the absorption unit nor within the absorption zone an inert gas is added. This way, the absorption process is very efficient since the gas phase contains less or no inert gas. Consequently, the dimensions of the absorption unit can be reduced, thereby saving investment costs, and a reduced volume of the absorption fluid, i.e. the solvent, can be used, with the effect that the amount of solvent to be recycled or processed in working-up stages can be considerably reduced, thereby improving the overall economics of the process.
- But although no inert gas is added prior to entering the absorption zone or in the absorption zone, safety of the process is ensured since the gas phase, although the oxygen content may be above the explosion limit, cannot be ignited.
- Preferably, the absorption unit is run as a bubble column.

According to a preferred embodiment, the gas bubbles dispersed in the continuous phase of the absorption solvent have a diameter of 10 millimeters or less, preferably 2 - 10 millimeters, most preferred 5 millimeters at the most.

According to a specifically preferred embodiment of the present invention, the gas stream is introduced into the absorption unit at a lower section of the absorption unit, and the liquid solvent phase enters the absorption unit at a position upwards with respect to the location the gas stream enters the absorption unit, and the liquid solvent phase exits the absorption unit at a position below the entry of the gas stream into the absorption unit. Thereby, it is achieved that the gas stream and the solvent pass through the absorption unit in a countercurrent manner. Preferably the absorption unit is run as bubble column.

The flow rate of the dispersed gas phase and of the continuous liquid solvent phase can be varied in wide ranges as long as the requirement that the liquid phase is continuous and the gas phase is dispersed is maintained. The flow rate per cross-section for the gas phase is preferably 10-100 m³/m²h, more preferred 20-60 m³/m²h and the flow rate per cross-section for the liquid phase is preferably 50 - 200 m³/m²h, more preferred 100 - 150 m³/m²h.

According to a preferred embodiment of the present invention, the gas stream is introduced into the absorption unit with a system of ring nozzles to finely disperse the gas phase in the continuous liquid phase. The dimensions of the absorption unit as well as the flow conditions of the gas phase and the continuous solvent phase are selected to provide gas bubbles dispersed in the continuous liquid phase having a diameter of 10 millimeters or less, preferably 2 - 10 millimeters, more preferred 5 millimeters at the most. Several measures can be taken singly or in combination to control the above defined bubbles size. For example the cross-section of the orifices of the ring nozzles can be selected to be within the range of 0.2 - 2 mm, and/or sieve trays can be positioned within the absorption unit in defined spacing having an orifice cross-section of 0.2 - 2 mm and/or the flow rate of the liquid phase and the

gas phase are adjusted as defined above. If sieve tray are used the ratio of the free cross-section of the sieve trays to the cross-section of the absorption unit is preferably adjusted to ensure a flow rate of the gas phase through the perforated plates of 0.5-2 m/s.

5

The absorption unit that can be used in the process of the present invention may comprise heat exchange means and/or gas dispersing means. Heat exchange means can be useful to control the temperature in the absorption unit, especially to remove the heat of absorption. Gas
10 dispersing means may be present to improve gas dispersion and the mass transfer between gas phase and continuous solvent phase. Preferably sieve trays and particularly preferably sieve trays with downcorners are used as gas dispersing means.

15

For safety reasons, it is preferred to introduce inert gas into the headspace above the liquid level within the absorption unit. Thereby, the gas stream exiting the liquid solvent phase is diluted to the extent that the oxygen concentration is below the explosion limit. Since the
20 gas phase after exiting the liquid solvent phase is no longer finely dispersed, the gas mixture will become ignitable in case the oxygen concentration due to depletion of combustible components during the absorption is above the explosion limit.

25 Any inert gas is suitable that has an oxygen content of less than 10 volume per cent and does not form combustible mixtures with oxygen. Preferred inert gas is nitrogen, carbon dioxide or water vapor or mixtures thereof, as may be obtained by usual combustion processes.

30 According to a preferred embodiment of the present invention no inert gas or only very limited amounts of inert gas are introduced into the gas stream prior to entering the absorption unit or into the absorption

zone within the absorption unit to achieve the reduction of absorption unit dimensions and volume of solvent. A suitable upper limit of the ratio of inert gas introduced into the gas stream prior to absorption or into the absorption zone is to oxygen present in the gas stream is 5 :

- 5 1. But it is preferred to introduce no inert gas into the absorption zone during the absorption process.

According to an alternative embodiment, the volume of the headspace in the absorption unit above the liquid level is reduced by displacers and
10 the absorption unit is equipped with pressure release means and a flame barrier in the gas exit line . In that case, the amount of inert gas introduced into the headspace can be considerably reduced while ensuring sufficient safety for the absorption process.

15 As continuous phase within the absorption unit, any liquid can be used that dissolves the combustible components that shall be recovered better than oxygen and that allows easy separation of the recovered components. Thereby, usual organic solvents like alcohols, aromatic and aliphatic hydrocarbons or ketones can be used. It is preferred to use a solvent
20 that is also used in the process the gas stream is derived from prior to the absorption. This is advantageous since then the solvent stream can be either directly recycled into the reaction zone or can be passed to a working-up stage downstream of the reaction stage.

25 In the process of the present invention, any gas stream from a reaction step wherein oxygen is generated and that contains combustible materials can be processed to recover valuable combustible components. It is particularly preferred that the gas stream is the gaseous effluent of an oxidation process using peroxide compounds. The process of the present
30 invention is especially preferred to recover olefin, and olefin oxide from the gaseous effluent from the epoxidation of an olefin with hydrogen peroxide.

Therefore, the present invention also refers to a process for the epoxidation of propene with hydrogen peroxide in an alcoholic solvent in the presence of a catalyst, wherein a gas stream comprising unreacted
5 propene, propene oxide, and oxygen from the decomposition of the hydrogen peroxide is separated from the reaction mixture and the combustible components in said gas stream are recovered using the process as described above.

- 10 According to a particularly preferred embodiment, the same alcoholic solvent as in the epoxidation step is also used in the recovery step. The preferred alcohol is methanol.

The pressure within the absorption unit in the recovery process

- 15 according to the present invention can be varied within wide ranges and can preferably be between atmospheric pressure and 50 bar, in case of absorption of propene and propene oxide the pressure is preferably within a range of 4-30 bar, more preferred between 10-25 bar.

- 20 The present invention will now be discussed in more detail with respect to the attached figure.

Figure 1 shows a suitable absorption unit for the present process in cross-section.

25

Figure 2 shows a preferred absorption unit according to the present invention in cross-section.

- Referring to Figure 1 a tubular absorption unit is shown, wherein the
30 gas stream 1 comprising combustible components and oxygen is introduced into the absorption unit through an inlet that is positioned near the lower end of the absorption unit. The inlet for the solvent stream 2

that forms the continuous liquid phase within the absorption zone is positioned closer to the upper end of the absorption unit. The outlet for the solvent 3 loaded with the absorbed combustible components is located at the bottom of the absorption unit. At the upper end of the
5 absorption unit, an inlet port is positioned to allow introduction of an inert gas 4 in order to dilute the gas prior to exiting the absorption unit to an oxygen concentration below the explosion limit. The exit gas stream 5 comprising oxygen, small amounts of combustible components, and optionally inert gas exits the absorption unit through an outlet
10 positioned at the top of the absorption unit.

Referring to figure 2 according to a preferred embodiment the gas stream 1 is introduced into the absorption unit through a system of ring
~~nozzles 9 to ensure efficient dispersion of the gas phase within the~~
15 continuous liquid phase. Within the absorption zone in the absorption unit, sieve trays 6 with downcomers are mounted to improve the mass transfer between the continuous phase and the dispersed gas to improve the absorption. The volume of the headspace above the fluid level at the upper end of the absorption unit is reduced by incorporation of
20 displacers 7 and a flame barrier 8 is positioned in the gas exit line.

The present invention will now be explained in more detail with reference to examples.

25 Example 1

A tube having a diameter of 76 millimeters and a length of 1,000 millimeters was filled with benzene and the temperature was maintained at 70°C. At the lower end, pure oxygen was injected at 4 bar pressure at a flow rate of 200 liters per hour. The portion of the gas phase within
30 the tubular absorption unit was 5 volume per cent as measured by the increase of the height of the liquid level. Due to the volatility of benzene, the uprising dispersed gas phase will be loaded with benzene

and immediately reaches an ignitable composition. A glow wire was immersed 10 centimeters below the liquid level, and it was tried to ignite the gas phase by applying an electrical pulse of 500 Watts. But no ignition of the dispersed gas phase could be observed.

5

Example 2

Example 1 was repeated with an oxygen flow of 170 liters per hour, while the portion of the dispersed gas phase within the liquid phase was 25 volume per cent. But also in this experiment, no ignition of the
10 dispersed gas phase could be observed.

The examples show that a gas phase containing a combustible material and oxygen in a ratio that is within the explosion range cannot be ignited as long as the gas phase is finely dispersed within a continuous liquid
15 phase.

Claims:

1. Process for the recovery of combustible components of a gas stream comprising the combustible components and oxygen by selective
5 absorption of the combustible components in a solvent, characterized in that during the absorption the gas phase is dispersed in a continuous liquid phase of the solvent.
- 10 2. The process of claim 1, characterized in that the process is a continuous process.
3. The process of any of the preceding claims, characterized in that
15 ~~the gas bubbles dispersed in the continuous phase have a diameter~~ of 10 mm or less, preferably of 5 mm at the most.
4. The process of any of the preceding claims, characterized in that
20 the gas stream is introduced into an absorption unit at a lower section of the absorption unit and the liquid solvent phase enters the absorption unit at a position upwards with respect to the
location the gas stream enters the absorption unit, whereby the
gas stream and the solvent pass through the absorption unit
25 counter-currently and the liquid solvent phase exits the absorption unit at a position below the entry of the gas stream into the absorption unit.
5. The process of any of the preceding claims, characterized in that the absorption unit is run as bubble column.

6. The process of any of the preceding claims, characterized in that the volume of the head space above the liquid level of the continuous phase is reduced by displacers.
- 5 7. The process of any of claims 4-6, characterized in that the gas stream exiting the liquid solvent phase is diluted with an inert gas to the extent that the oxygen concentration is below the explosion limit.
- 10 8. The process of claim 7, characterized in that the inert gas is selected from nitrogen, water vapor, carbon dioxide or mixtures thereof.
-
- 15 ~~9. The process of any of claims 4-8, characterized in that~~
the gas stream is introduced into the absorption unit through a system of ring nozzles.
- 20 10. The process of any of claims 4-9, characterized in that the flow conditions within the absorption unit are selected to provide gas bubbles dispersed in the continuous liquid phase having a diameter of 10 mm or less, preferably of 5 mm at the most.
- 25 11. The process of any of claims 4-10, characterized in that the absorption unit comprises heat exchange means and/or gas dispersing means.
- 30 12. The process of claim 11, characterized in that sieve trays are positioned within the absorption unit.

13. The process of any of the preceding claims, characterized in that the gas stream is the gaseous effluent of an oxidation process using peroxide compounds.
- 5
14. The process of any of the preceding claims, characterized in that the solvent is selected from alcohols, aliphatic and aromatic hydrocarbons and ketones.
- 10 15. A process for the epoxidation of propene with hydrogen peroxide in an alcoholic solvent in presence of a catalyst, wherein a gas stream comprising unreacted propene, propene oxide and oxygen from the decomposition of the hydrogen peroxide is separated from the ~~reaction mixture and the combustible components in said gas stream~~
- 15 are recovered using a process according to any of claims 1-14.
16. The process of claim 15, wherein in the recovery step the same alcoholic solvent as in the epoxidation step is used.
- 20 17. The process of claim 16, wherein the solvent is methanol.
18. The process of any of claims 16 and 17, wherein the liquid solvent phase comprising the recovered combustible components is either recycled to the epoxidation step or is passed to a working up
- 25 stage downstream from the epoxidation step.

1 / 1

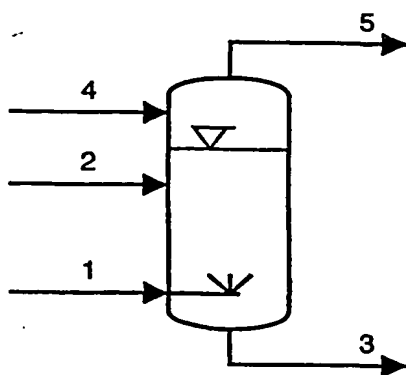


Fig. 1

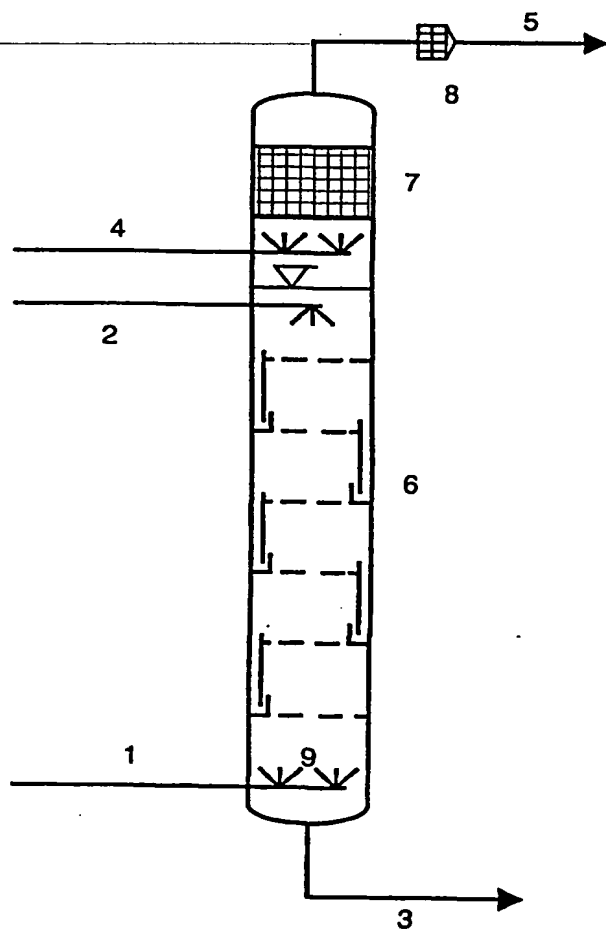


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/06448

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/14 B01D53/18 C07D301/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 583 828 A (THE DOW CHEMICAL COMPANY) 23 February 1994 (1994-02-23) column 2, line 35 -column 6, line 23	1,2,4,7, 12-14
X	EP 0 719 768 A (ARCO CHEMICAL TECHNOLOGY) 3 July 1996 (1996-07-03) cited in the application column 2, line 3 -column 4, line 51	1,2, 14-16,18
A	EP 0 827 765 A (NIPPON SHOKUBAI CO, LTD.) 11 March 1998 (1998-03-11) column 2, line 5 -column 2, line 24	15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *G* document member of the same patent family

Date of the actual completion of the international search

5 November 2002

Date of mailing of the international search report

11/11/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Bogaerts, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/06448

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 583828	A	23-02-1994	US 5233060 A	03-08-1993
			CA 2103973 A1	14-02-1994
			DE 69302342 D1	30-05-1996
			DE 69302342 T2	28-11-1996
			EP 0583828 A2	23-02-1994
			JP 2972496 B2	08-11-1999
			JP 7053536 A	28-02-1995
EP 719768	A	03-07-1996	US 5468885 A	21-11-1995
			DE 69508051 D1	08-04-1999
			DE 69508051 T2	15-07-1999
			EP 0719768 A1	03-07-1996
EP 827765	A	11-03-1998	JP 10146523 A	02-06-1998
			JP 10118473 A	12-05-1998
			EP 0827765 A2	11-03-1998
			TW 393339 B	11-06-2000
			US 6123323 A	26-09-2000